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John S. Sanders, Branch Chief

Department of Pesticide Regulation

Environmental Monitoring and Pest Management

Date

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Place

Sacramento

Phone:

324-4 137

Randy Segawa, Sr. Env. Res. Scientist

Terri Barry, Assoc. Env. Res. Scientist

Pam Wofford, Assoc. Env. Res. Scientist

Environmental Hazards Assessment Program

Subject: Methyl Bromide Monitoring: Building Fumigation, Stanislaus County

This study measured the air concentrations associated with a methly bromide fumigation of a building, estimated the size of buffer zones required for this type of fumigation and how the measured concentrations compared with those predicted by a computer simulation model.

A total of 2175 pounds of methyl bromide were used to treat a 1,450,000 cubic foot building. The treatment period was approximately 24 hours. At the end of the treatment period, several doors were partially opened and three roof vents were turned on. Downwind air samples were collected at 15 locations, using charcoal tubes. Air concentrations inside the building were measured with a Fumiscope during the treatment period, and aeration. The measured concentrations were compared to the concentrations predicted by the Industrial Source Complex-Short Term (ISCST) model. During the treatment period, the highest 23-hour average concentration detected was 0.43 ppm. Measurements of air concentrations inside the building indicate that at least 59% of the applied methyl bromide was retained within the structure during the 23-hour treatment period. Average concentrations as high as 6.44 ppm were detected during the first hour of aeration. It was estimated that a buffer zone of 670 feet would have been required during treatment and a buffer zone of 300 feet would have been required during aeration.

The ISCST model generally performed well. Using the site specific data, the model did not display any bias. A detailed description of the monitoring and modeling is attached.

Approved:

Branch Chief

Date

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Segawa

Wilfoul Barry

Introduction - The objectives of this monitoring were to measure the air concentrations associated with a methyl bromide fumigation of a building, estimate the size of buffer zones required for this type of fumigation and how the measured concentrations compared with those predicted by a computer simulation model. Building fumigations can use a large amount of methyl bromide because of the large volume that must be fumigated and leakage of an unknown fraction of the applied methyl bromide.

Materials and Methods - The building fumigated was a large food processing plant, with each side 200 feet long, one section 28 feet tall and a second section 48 feet tall. The procedures used to fumigate this facility were fairly common. All doors and other openings were sealed with plastic tarp prior to the fumigation. Methyl bromide was introduced into the structure on April 8, 1993, 5:45 PM. A total of 2175 pounds of methyl bromide were used to treat the 1,450,000 cubic foot building (application rate 1.5 lbs/1000 ft³, 6200 ppm). The treatment period was approximately 24 hours. At the end of the treatment period, several doors were partially opened and three roof vents were turned on. Each roof vent had a 57 inch diameter fan with a height of 68 inches above the roof and a rated fan capacity of 10,000 cubic feet per minute. The aeration period was an additional 24 hours.

Downwind air samples were collected at 15 locations using charcoal tubes and SKC air samplers calibrated at 15 ml/min. Eight of the sampling locations were 30 feet from building and seven were 100 feet from the building (Figure 1). Four, six-hour samples were collected at each location during the treatment period. These were followed by four, 15-minute samples during the aeration (aeration and sampling were started simultaneously). Aeration samples were collected at six downwind locations, three at 30 feet and three at 100 feet (Figure 2). The California Department of Food and Agriculture's Chemistry Laboratory Services determined the amount of methyl bromide in the charcoal tube samples by extracting with ethyl acetate and analyzing with a gas chromatograph/electron capture detector. Wind speed, wind direction, temperature and humidity were recorded at one minute intervals with a Met-1 [®] station located at the site.

Air concentrations inside the building were measured with a Fumiscope during the treatment period and aeration. Stack air concentrations were also measured at one of the roof vents during aeration.

The measured concentrations were compared to the concentrations predicted by the Industrial Source Complex-Short Term (ISCST) model. This model uses the emission rate, emission characteristics (dimensions, emission height), weather conditions (wind direction, wind speed, atmospheric stability), and terrain characteristics (urban or rural) to estimate the downwind air concentrations.

Results - During the treatment period, leakage of methyl bromide from the building caused ambient concentrations to exceed the 0.21 ppm (24-hr time weighted average, TWA) target **level. Measurements of air concentrations inside the building indicate that at least 59% of the** applied methyl bromide was retained within the structure during the 24-hour treatment

period, as estimated by linear regression (Table 1). Since most of the building was empty, it is likely that there was minimal absorption of the applied methyl bromide. Therefore, up to 41% of the methyl bromide leaked out of the building during the treatment period. This lead to methyl bromide being detected downwind from the building. During the treatment period, the highest 23-hour TWA detected was 0.43 ppm (Table 2). Figure 1 shows the expected geographic pattern of air concentrations, with the highest concentrations located along the predominant wind direction, and concentrations decreased with distance from the source.

Downwind air concentrations measured during the aeration indicate that the building itself had a significant influence on the local wind patterns because high concentrations were detected 30 feet from the building (Figure 2). Normally, methyl bromide released through a roof stack would be carried away from the building and not reach ground level for some distance downwind. Building downwash carried methyl bromide from the exhaust stacks to ground level very rapidly. Average concentrations as high as 6.44 ppm were detected during the first hour of aeration (Table 3), exceeding the 5 ppm (1-hr TWA) target level. Methyl bromide levels measured at one of the exhaust stacks still exceeded 1000 ppm at the end of the monitoring period (Table 4). Therefore, high downwind concentrations would be expected to continue past the one hour monitoring period.

The measured concentrations were compared to the concentrations predicted by the ISCST model. The treatment and aeration periods were modeled as separate events. For the treatment period, the fumigation was modeled as an area source, with an emission rate determined from the air concentrations measured inside the building. Initially, the treatment period was modeled as a single area source with a height of 3 feet. Regression of the predicted and measured values showed that the model tended to overestimate the measured concentrations (slope 1.86, intercept -0.14). Therefore, other combinations of emission height were simulated. The combination of one source at three feet and one source at roof height (25 feet) resulted in concentrations closest to the measured values (Table 5). The following regression of measured versus modeled concentrations indicates how well the modeled performed:

modeled =
$$1.14$$
(measured) - 0.09 $R^2 = 0.42$

The ISCST model gave a closer prediction for the aeration period (Table 5). This phase was modeled as a stack source. The emission rate was estimated using the measured stack air concentration and air flow based on the rated fan capacity. Normally, the exhaust fans do not achieve their rated capacity because not enough make-up air is provided and/or they are connected to long ducts. However, in this case the fans were located at the top of the stack and it was assumed that the air flow was close to the rated capacity. Two of the sites that had measurable concentrations could not be modeled (East 30 and 100) because they were located too close to the building. The following regression of measured versus modeled concentrations indicates how well the model performed:

modeled = 1.11 (measured) – 1.45
$$R^2 = 0.77$$

Using the ISCST model to estimate the measured concentrations, the furthest distances at which 0.21 ppm (24-hr TWA) occurred were 670 feet and 300 feet for the treatment and aeration, respectively.

Conclusions - This structure was a concrete building which had all large leakage areas such as doors and vents **tarped** and sealed before fumigation. Therefore, this building could be expected to retain more methyl bromide than some other building types, for example those constructed of corrugated metal. Despite the good construction and sealing there was still enough leakage during the treatment period to cause an inadequate margin of safety for a 24 hour exposure 100 feet from the building.

During the aeration, the stack heights were apparently too low (6 feet above the roof) to avoid downwash created by the building. This lead to high levels of methyl bromide detected 30 and 100 feet from the building throughout the monitoring period. In addition, detectable emissions and downwind air concentrations were measured during the last monitoring period (60 minutes after the start of aeration). The rate of decline indicated that detectable concentrations would continue to be found for several hours. Therefore, the actual 24-hour TWA concentrations and required buffer zone size would be higher than those documented here.

The ISCST model generally performed well. Using the site specific data (emission rate, emission source dimensions, weather), the model did not display any bias, since the modeled concentrations were lower than the measured concentrations in 7 cases and higher in 4 cases. However, in order to calculate buffer zones which encompass all types of facilities, all of the site specific information cannot be used. In particular, default assumptions must be made regarding weather conditions and source dimensions, two factors which significantly influence the size of the buffer zone. Depending upon the assumptions used, the resulting buffer zones may be much larger than needed for the great majority of fumigations. Some flexibility in the size of the buffer zones can be provided by using site specific application rates, size of volumes fumigated, and proportion of methyl bromide retained.

Table 1. Methyl bromide concentrations inside building during the treatment period

	Upper Sampling	Lower Sampling	Average
Date/Time	Point (ppm)	Point (ppm)	(ppm)
4/8/93/2000	5900	7700	6800
4/9/93/0000	5700	5700	5700
4/9/93/0600	5200	4900	5000
4/9/93/1200	4400	4100	4300
4/9/93/1625	3900	3400	3600

Table 2. Ambient methyl bromide concentrations during the treatment period

Sample Location		Methyl Bromide (ppm) During Each Sampling Period				
Transect	Distance	1745-2345	2345-0545	0545-1 145	1145-1630	23-hr TWA*
N	30	ND**	ND	ND	ND	ND
N	100	ND	ND	ND	ND	ND
NW	30	ND	ND	ND	ND	ND
NW	100	ND	ND	ND	ND	ND
\mathbf{W}	30	ND	ND	ND	ND	ND
\mathbf{W}	100	ND	ND	ND	ND	ND
SW	30	ND	ND	ND	ND	ND
SW	100	ND	ND	ND	ND	ND
S	30	0.41	0.25	0.22	0.17	0.26
S	100	0.33	0.18	0.14	0.12	0.20
SE	30	0.50	0.51	1.03***	0.24	0.43
SE	100	0.50	sample lost	0.34	0.17	0.34
E	30	0.40	0.29	0.34	0.24	0.33
Е	100	0.19	0.34	0.24	0.23	0.24
NE	30	0.02	ND	ND	ND	0.007

^{* 23-}hour time weighted average (TWA)

^{**} None Detected, detection limit approximately 0.006 ppm

^{***} Sampler shut down early

Table 3. Ambient methyl bromide concentrations during the first hour of aeration. Aeration started at 17:07.

Sample Location		Methyl Bromide (ppm) During Each Sampling Period				
Transect	Distance	1707-1722	1722-1737	1737-1752	1752-1807	1-hr TWA*
E	30	1. 03	0. 81	0.20	0. 18	0. 55
E	100	0.97	0. 20	0.04	0. 20	0. 35
SE	30	6. 50	3.39	1.29	1.77	3. 24
SE	100	12.93	6.21	2.09	2.94	5.99
S	30	14.98	5.97	3.18	1.69	6. 44
S	100	7. 27	3. 22	1.96	0.99	3. 36

^{*} l-hour time weighted average

Table 4. Methyl bromide concentrations within the exhaust stack during aeration

	Methyl	
	Bromide	
Sampling Period	(ppm)	
1707 - 1710	3400	
1710-1713	3190	
1713 - 1716	4010	
1716 - 1719	2850	
1719 - 1722	2820	
1722-1727	2550	
1727-1737	1870	
1737 - 1752	1360	

Table 5. Comparison of methyl bromide concentrations measured in the field to those predicted by the ISCST model

Sample Location		Methyl Bromide (ppm)*		
Transect	Distance	Modeled	Measured	
Treatment				
S	100	0.080	0.26	
S	30	0.19	0.20	
SE	30	0.56	0.43	
SE	100	0.52	0.34	
E	30	0.023	0.33	
E	100	0.021	0.24	
NE	30	0.022	0.01	
Aeration				
S	30	6.14	6.44	
S	100	1.13	3.36	
SE	30	3.32	3.24	
SE	100	4.74	5.99	

^{*} Treatment concentrations are 24-hour averages, aeration concentrations are

¹⁻hour averages.

Figure 1. 24-Hour Average Measured Concentrations (ppm) During Fumigation.

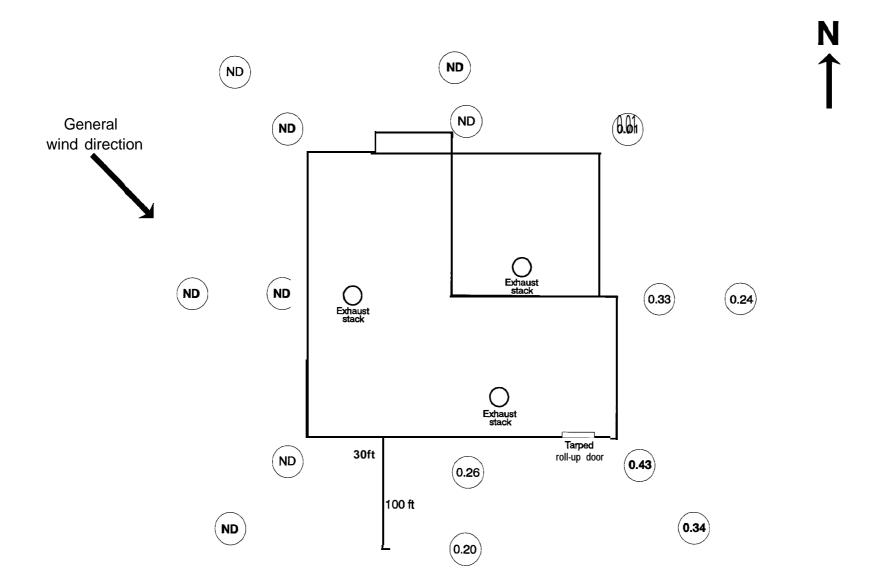


Figure 2. Average Measured Concentrations (ppm) During First Hour of Exhaust.

